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Short communication

Effective solution resistivity in beds containing one monolayer or multilayers of uniform spherical glass beads

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1. Introduction

Electrolysers with parallel-plate electrodes are used industrially to produce gases like hydrogen, oxygen and chlorine. The bubble layer adjacent to a gas-evolving electrode consists of two sublayers, namely, the first sublayer with bubbles attached to the electrode surface and the second sublayer with rising bubbles [1].

The diameter of the attached bubbles determines the thickness of the first sublayer, mostly in the range from 10 to 100 μm, depending on many parameters: for example, nature of gas evolved, composition of solution, solution flow rate and current density [1, 2]. The thickness of the second sublayer is much larger; under industrial conditions a thickness of a few millimetres [3]. The ohmic voltage drop in a gas-evolving electrolyser is mainly determined by the presence of bubbles in the solution. Numerous investigations have been carried out to describe the effect of the volume fraction, ε, of nonconducting particles on the effective resistivity of a mixture of nonconducting particles and a conducting solution.

A short review on the effective resistivity of a mixture of two phases was published by Vogt [4]. Various mathematical relationships have been derived for different geometries of the nonconducting dispersed phase by Maxwell [5], Rayleigh [6], Fricke [7], Runge [8], Meredith and Tobias [9], Neale and Nader [10] and Bruggeman [11]. Almost all give practically the same result for the increase in resistivity as a consequence of the increasing volume fraction ε of the nonconducting phase of the mixture at $\varepsilon < 0.1$, but show clearly different results at high ε, that is, $\varepsilon > 0.4$.

The relation $R/R_p = (1-\varepsilon)^{-3/2}$ presented by Bruggeman, is widely applied to describe the effect of bubbles on the resistivity of a bubble containing solution, and the current distribution in a gas-evolving electrolyser, where R is the solution resistance in the presence of beads and R_p is the resistance of the pure solution. Experiments on suspensions of nonuniform spherical glass beads with $\varepsilon < 0.4$ were carried out by De La Rue and Tobias [12]. These indicated that Bruggeman's approximation satisfactorily represented the dependence of the effective resistivity on the volume fraction ε, with the dispersed phase containing a broad particle size range. Their experiments were performed with homogeneous swarms of spherical particles, obtained by continuously agitating the particle solution mixture such that the position of each particle changes.

The bubbles in the first bubble sublayer at a gas-evolving electrode can be considered as bubbles attached to the electrode surface on fixed positions. To simulate a first bubble sublayer, a layer of glass beads with an almost uniform diameter was placed between two horizontal flat plate electrodes. The ohmic resistance of the solution layer with a single bead layer was determined and compared to the results predicted by various mathematical relationships. Moreover, the ohmic resistance of the solution was determined for a bed containing several layers of such beads.

2. Experimental details

The electrolysis cell used is schematically represented in Figure 1. The thermostated cell was a glass cylinder with an inner diameter of 3.81 cm and a height of 8 cm. All experiments were carried out at 218 K. The base of the cell was formed by a flat nickel plate which served as the lower electrode. A 0.5 mm thick silicone ring which also had an inner diameter of 3.81 cm was placed between the glass cylinder and the base electrode. The other electrode, the top electrode, was also a flat nickel plate with a diameter very slightly smaller than 3.81 cm, so that this electrode, on which a nickel wire with a length of 15 cm had been welded, could be moved up and down inside the cell. The top electrode had four cylindrical holes with a diameter of 0.4 cm to prevent the disturbance of the top layer of beads by liquid convection (particularly for beads with a small diameter). This convection took place when the top electrode was put on the glass beads bed. Both electrodes were placed horizontally and parallel to each other.

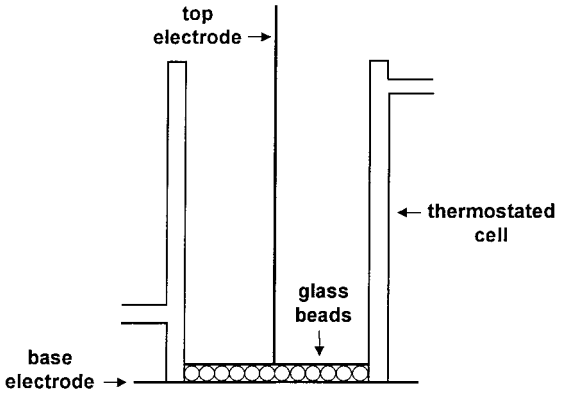

Fig. 1. Schematic diagram of electrolysis cell.

Experiments were carried out with either a small number of beads (the exact number depending on the bead size), a near monolayer of glass beads or with different monolayer portions of beads corresponding to up to nine monolayers. Special care was paid to the number of beads in the cell and to the position of the top electrode; this electrode had to be parallel to the base electrode. A sufficient quantity of a KCl solution was added to the cell to obtain a solution level which was about 2 cm higher than the top electrode. The experiments were carried out at 298 K and with KCl solutions of concentration 0.01, 0.1, 0, 3, 1.0 and 4.0 M.

Spherical glass beads were used. The diameter ranges selected for this study were 1.7–2.1 ('2'), 2.7–2.9 ('3'), 5.7–5.9 ('6') and 11.9–12.2 mm ('12'). The beads were cleaned thoroughly.

The impedance measurements were carried out galvanostatically with a Solartron 1286 Electro Chemical Interface combined with a Solartron 1250 frequency response analyser. The impedance spectra were taken in the frequency range 100 Hz to 65 kHz.

3. Results and discussion

The impedance spectra showed a well-shaped semicircle in the Bode plot; the ohmic resistance of the solution between the base and top electrode was accurately determined from this plot. The scatter in the ohmic resistance data was very small. The contribution of the measurement wires to the experimental resistance R_{exp} was negligible. Experiments with various KCl concentrations were carried out with either three '6 mm' beads, or with 30 '6 mm' beads, the latter resulting in an almost complete monolayer. From the results of the experiments with only three beads the resistance of the bead-free solution, R_p, between the electrodes was calculated using the Bruggeman relation. It was found that in this case $R_p = 0.93\ R_{exp}$, where R_{exp} is the experimental value. The difference between R_p and R_{exp} is small because of the low bed volume fraction ε (i.e., 0.048), where the use of the Bruggeman relation is acceptable, since all relations presented in the literature give near identical results for $\varepsilon < 0.1$ [1].

Table 1. Experimental voidage factor (X_{exp}) for an almost complete monolayer of '6' mm beads in KCl solutions with various concentrations C_{KCl} and at 298 K

C_{KCl}/M	X_{exp}
0.01	2.84
0.1	2.74
0.3	2.75
1	2.20
4	1.75

Table 1 summarizes the data obtained for an almost complete monolayer of '6 mm' beads ($\varepsilon = 0.481$). The table shows the ratio R_{exp}/R_p, called the voidage factor (X_{exp}), in KCl solutions of various concentrations. From this table it follows that X_{exp} is practically constant at $C_{KCl} \leq 0.3$ M, and decreases strongly with increasing C_{KCl} at higher concentrations. The dependance of X_{exp} on the KCl concentration is remarkable and unexpected. It may be possible that the Helmholz double layer at the surface of the beads enhances the overall conductivity of the solution in the bed, so that additional transport of ions along the beads takes place.

Calculations have shown that the voidage factor X_B, being $(1 - \varepsilon)^{-1,5}$ according to the Bruggeman relation, is 2.67, the factor X_R, being $(1 + 0.5\ \varepsilon)/(1 - \varepsilon)$ according to the Rayleigh relation, is 2.39, and the factor X_M, being $1 - 1.78\ \varepsilon + \varepsilon^2$ according to the Mashovets relation, is 0.375 [13].

Comparing the experimental X_{exp} with the calculated X_B, X_R and X_M, it is concluded that the Bruggeman equation gives the best fit and that the Mashovets relation can be rejected.

The effect of bead size on the voidage factor for an almost complete monolayer was investigated for a 0.1 M KCl solution at 298 K. As described previously, R_p was obtained from measurements at a low ε, namely, 0.010, 0.024, 0.048 and 0.072 for, respectively, '2', '3', '6' and '12' mm beads. In the case of '12' mm beads only one bead was used to prevent a too high ε in the experiment obtaining R_p.

In Table 2 the bead voidage, ε, the resistance R_p of the bead-free solution between the electrodes, the resistance R_{exp} for a bed of an almost monolayer of beads, the experimental voidage factor X_{exp} and only the calculated X_B and X_R are given for various bead sizes since X_M is

Table 2. Voidage ε and resistances R_p and R_{exp} for a bed of a near monolayer of beads with experimental X_{exp} and calculated X_B and X_R given for various bead sizes in 0.1 M KCl at 298 K

Bead size/mm	ε	R_p/Ω	R_{exp}/Ω	X_{exp}	X_B	X_R
'2'	0.582	1.842	6.25	3.39	3.70	3.09
'3'	0.529	2.363	7.18	3.04	3.09	2.68
'6'	0.481	4.043	11.26	2.79	2.67	2.39
'12'	0.503	8.586	26.20	3.05	2.85	2.52

much higher than X_B. By calculation it was found that the maximum voidage, ε_{max}, for a monolayer of uniform spherical beads is 0.605. Comparing ε_{max} with ε from Table 2 it is concluded that ε for the '2' mm beads is almost equal to ε_{max}. This means that presumably the distance between the two electrodes is slightly higher than the maximum diameter of the '2' mm beads. It was calculated that X_{exp} and X_B can be equalized, assuming an approximately 10% higher electrode distance for the monolayer experiment than the maximum diameter of the '2' mm beads. For the experiments with the other bead sizes it is likely that each bead is in contact with the base electrode.

From Table 2 it follows that X_{exp} and X_B give the smallest difference; in particular for the '3' mm, '6' mm and '12' mm beads. Moreover, there is no reason why the particle size should have any effect on the voidage factor [12]. It is concluded that the Bruggeman relation is very useful for determination of the resistance of the solution in a fixed bed formed by a monolayer of uniform spherical particles.

Sides [14] has carried out similar experiments in a hexagonal cell; this cell accomodates a 10.16 cm diameter sphere, at the maximum, which represents close packing. From the experimental results with only one sphere with a diameter in the range 5.84–10.16 cm in the hexagonal cell it can be shown that for voidages from 0.200 to 0.605 the difference between X_{exp} and X_B is in the order of 10%.

A series of experiments with various layers of '6' mm beads were carried out with a 0.1 M KCl solution. An almost complete monolayer was obtained by using 32 beads, where ε was 0.507, being smaller than ε_{max} (i.e., 0.605). Portions of 32 beads were added to the cell and thereafter the top of the bed was equalized and the top electrode was placed horizontally on the top beads.

In Figure 2 the experimental R_{exp} is given versus the number of bead layers added to the cell. Figure 2 shows that R_{exp} is linearly proportional to the number of monolayers of beads forming the bed, and thus to the height of the bed. An experiment was carried out with a bead-free cell in which the top electrode was placed in the same position as in the experiment with 288 beads corresponding to the 9 layer test. From volumetric measurements it was found that $\varepsilon = 0.593$. This value is smaller than that (i.e., 0.680) for a body-centred cubic structure and larger than that (i.e., 0.524) for a simple cubic structure of uniform beads [15]. It was found that for the 288-bead bed the voidage factor X_{exp} was 3.34, whereas the voidage factor predicted by the Bruggeman equation was 3.85. The agreement between X_{exp} and X_B is reasonable. Consequently, the ohmic resistance of solution within a fixed bed of uniform spherical particles can be well described by the Bruggeman relation. From the preceding results it can be concluded that the effective resistance of the solution, both in the first bubble sublayer and in the second bubble sublayer at a gas-evolving electrode, is well described by the Bruggeman relation.

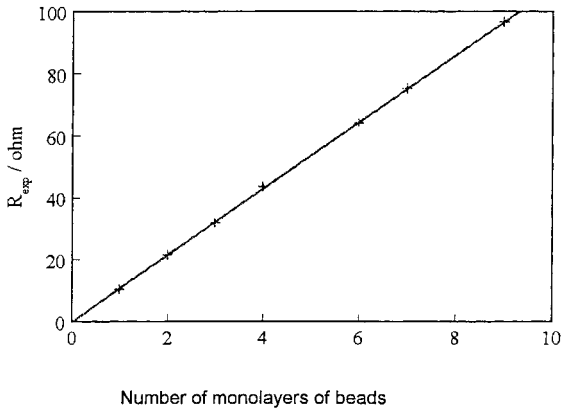

Fig. 2. Ohmic resistance of the solution between the base and the top electrode as a function of the number of monolayer of beads for a 0.1 M KCl solution and at 298 K.

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